Russian Journal of Aquatic Ecology, 2(2), 1993, pp. 123-130

THE DISSOLVED ORGANIC MATTER OF THE BERING SEA

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ABSTRACT. Data on the horizontal and vertical distribution of the dissolved organic carbon (C_{org}) are presented. The concentrations of dissolved C_{org} were determined by high-temperature catalytic oxidation under oxygen atmosphere on TOC-500. The obtained values ranged from 1.5 to 6.0 mgC/L. There were few minimal concentrations observed. The spatial distribution is fairly patchy and generally depends on the rates of primary production and destruction of organic matter. The physico-chemical nature of the flocculation process apparently influences the distribution of dissolved C_{org} in the Anadyr Bay. The dissolved organic matter of the Bering Sea is hard to be completely oxidized. Easily hydrolyzed fraction makes up no more that 30%. Carbon of high-polymeric nitrogen compounds, i.e. proteins and nucleic acids, is the most resistant to complete oxidation.

Key words: dissolved organic matter, dissolved organic carbon, spatial distribution, Bering Sea.

Introduction

All the investigators of the Bering Sea noted the high rates of primary and secondary production as its characteristic feature of its ecosystem. The Bering Sea productivity could be compared with that of the upwelling zones of the Pacific and Atlantics (Issledovanye ekosistem... 1990, Hansel et al. 1989, Results of the third... 1992, Walsh 1988, Walsh and McRoy 1986). Therefore, studies in organic matter (OM) and its spatial and temporal variability become of a particular importance, helping on the one hand to evaluate energy supply for the development of heterotrophic life, and, on the other, to identify the changes of OM in the process of its utilization by the community. A great amount of dissolved and particulate OM, via bacterial pump is transported as a «primary food» to higher trophic levels in the Bering Sea. Thus, the assessment of dissolved organic matter (DOM) and particulate organic matter (POM) stocks is essential for the determination of the waters trophy and the values of biological productivity.

Unfortunately, the content of organic carbon (C_{org}), both dissolved and particulate, which closely reflects OM concentrations of the Bering Sea, was scarcely measured. There are some data on the distribution of dissolved and particulate C_{org} in the northeastern Bering Sea and the Chukchi Sea (Loder 1971, Kinney et al. 1971), as well as more recently obtained data on the western part of the Bering Sea (Ljutsarev et al. 1988, Pashkova et al. 1988). In 1984 and 1988 the joint Soviet-American investigations were aimed at more comprehensive study of POM in all basic ecological subsystems of the Bering Sea (Issledovanye ekosistem... 1990, Hansel et al. 1989, Results on the third... 1992, Whitledge et al. 1988). Data on dissolved OM are also unsatisfactory, as the analysis methods used during the above-mentioned investigations could not provide complete oxidation of C_{org} in all organic compounds.

The present investigations were aimed at the assessment of distribution of DOM in the ecosystems of shelf and open waters of the Bering Sea. The goal aim of the studies could be gained only through precise technique of analysis of the concentrations of dissolved C_{org}.

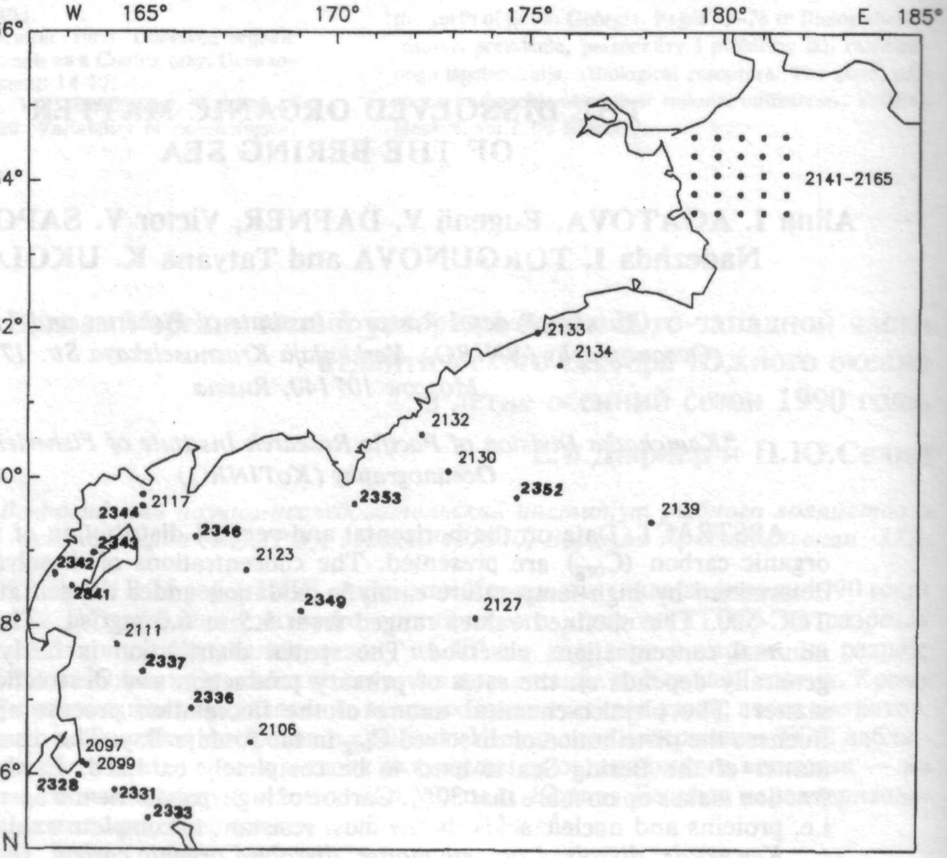


Fig. 1. Location of stations.

Materials and methods

The present paper introduces results of studies on the horizontal and vertical distribution of dissolved C_{org} in the shelf and deep waters of the northwestern Bering Sea from the Kamchatka Strait to the Anadyr Bay. The measurements were carried out during the 21st and the 24th cruises of R/V «Akademik Nesmeyanov» in June, 1992, and July, 1993, respectively.

The choice of stations was determined by the target to compare regions of different productivity: the shelf waters, the deep waters, and the areas important for commercial fisheries, e.g. the Kamchatka Strait and the Karagin shelf. The Anadyr Bay was of a special interest because of the pattern of dissolved OM distribution formed under the influence of mixing processes of the river discharge and sea waters. Fig. 1 shows the location of stations where assessment of dissolved C_{org} was undertaken.

The sampling was performed with a CTD probe Neil Brown. Parallel measurements of the vertical changes in salinity, temperature, dissolved oxygen and chlorophyll *a* concentrations (by the intensity of fluorescence) were carried out. The CTD profiler was equipped with a set of 20 Niskin plastic bottles (1.7 L). In deep waters the sampling was performed in the water column to the depth of 1000 m. According to the extreme values registered by the probe a certain number of bottles were closed at each depth. Samples were generally taken at 10 horizons in the deep waters. In shallow and shelf waters the samples were, as a rule, taken in two layers: the surface and the bottom, with additional one, the intermediate layer, when a maximum of oxygen or chlorophyll was registered.

To remove mesoplankton cells the water samples from 2 to 3 bottles closed at the same depth were poured through the 60 μm gauze into a plastic flask. Then the water was filtered through a glass fiber filter GF/F. The filtrate with particles of >0.2 μm was used to determine the dissolved C_{org} content.

During the 21st cruise of R/V «Akademik Nesmeyanov» concentrations of dissolved C_{org} were determined with an AutoAnalyzer «Technicon». The DOM organic carbon was UV irradiated and then oxidized by potassium persulphate (Collins and Williams 1977). In our previous papers it has been shown that this method does not lead to the complete oxidation of C_{org} to CO_2 and H_2O and the results depend on the composition and quality of the OM (Torgunova et al. 1992). Consequently, a complex standard

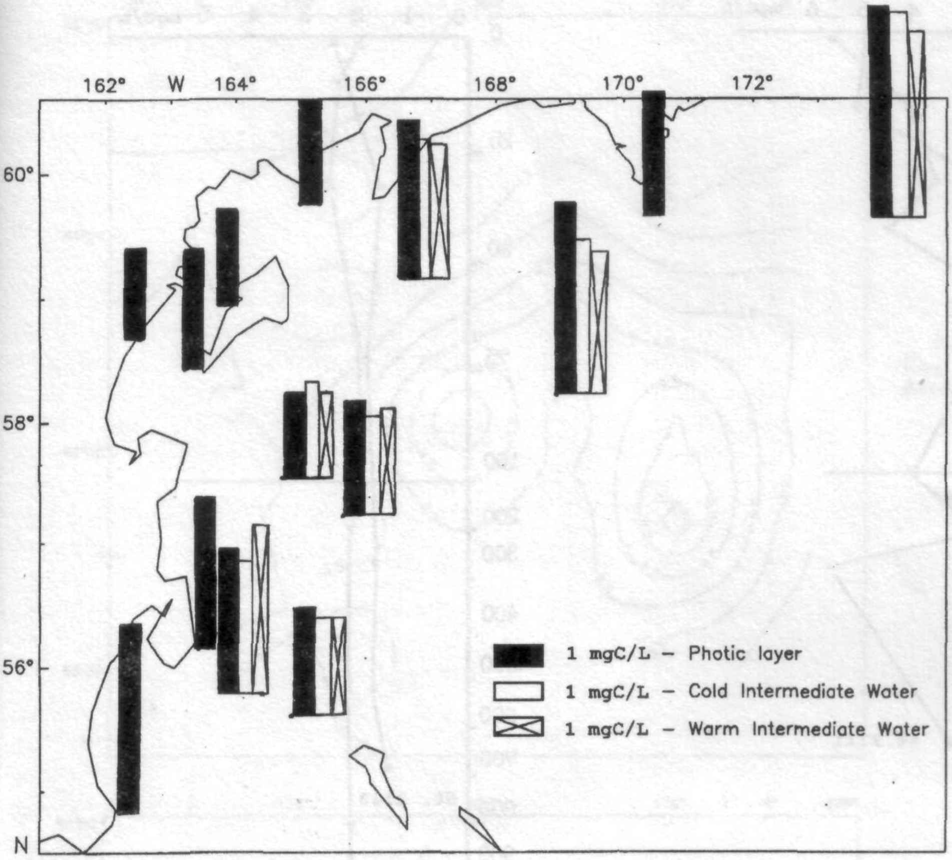

162°
W
164°
166°
168°
170°
172°
60°
58°
56°
N
1 mgC/L – Photic layer
1 mgC/L – Cold Intermediate Water
1 mgC/L – Warm Intermediate Water

Fig. 2. Mean concentrations of dissolved C_{org} in the photic layer, CIW and WIW (mgC/L).

for C_{org} analysis was prepared. A mixture of organic substances (glucose, proteins and nucleic acids in the 2 : 1 : 1 ratio) was assumed similar to the OM composition in the sea water. The Bering Sea OM presents a problem for oxidation analysis. Thus, in order to get better results the water samples were preliminary hydrolyzed under «tough» conditions (the samples were boiled with 2N H_2SO_4, or with 1N NaOH for 30 min to adjust them to pH 4.5-5.0.

In 1993, during the 24th cruise of R/V «Akademik Nesmeyanov», the dissolved C_{org} was determined by two methods to compare the completeness of oxidation: 1) using an Auto Analyzer «Technicon» with the preliminary hydrolysis (the method used in 1992), and 2) a high-temperature oxidation (680°C) using a platinum catalyst under oxygen atmosphere (Sugimura and Suzuki 1988) on TOC-500 «Shimadzu».

The high-temperature catalytic process on TOC-500 results in the complete oxidation of DOM of any composition. Consequently, the system could be calibrated with a simple standard: either with potassium phthalate, or glucose. No preliminary hydrolysis is needed. Still, because of the sea water high concentrations of carbonates we had to expel inorganic carbon prior to the determination of dissolved C_{org}. The samples were acidified with HCl and inorganic carbon was expelled by an air stream without CO_2 for 10 min.

The use of two techniques resulted in more reliable data on DOM content in the Bering Sea.

Results

Spatial distribution of dissolved C_{org} is rather patchy both horizontally and vertically. The concentrations of dissolved C_{org} ranged from 6.0 to 1.5 mgC/L. No definite trends of dissolved C_{org} distribution were observed. Thus, high values of C_{org} (3.0-4.0 mgC/L) were obtained in shelf waters of the Kamchatka Strait, while the Karagin shelf waters were characterized by concentrations 1.5-2.0 times lower. The shelf waters to the north of the Kamchatka Strait and up to the Shirshov Chain were characterized by a gradual increase in C_{org} content northeastwards. A similar increase in dissolved C_{org} concentrations was observed at deep water stations not only in the photic layer, but also in the Cold Intermediate Water and Warm Intermediate Water. Such a phenomenon could be explained by the northeastward increase in primary production, and, consequently, in zooplankton biomass.

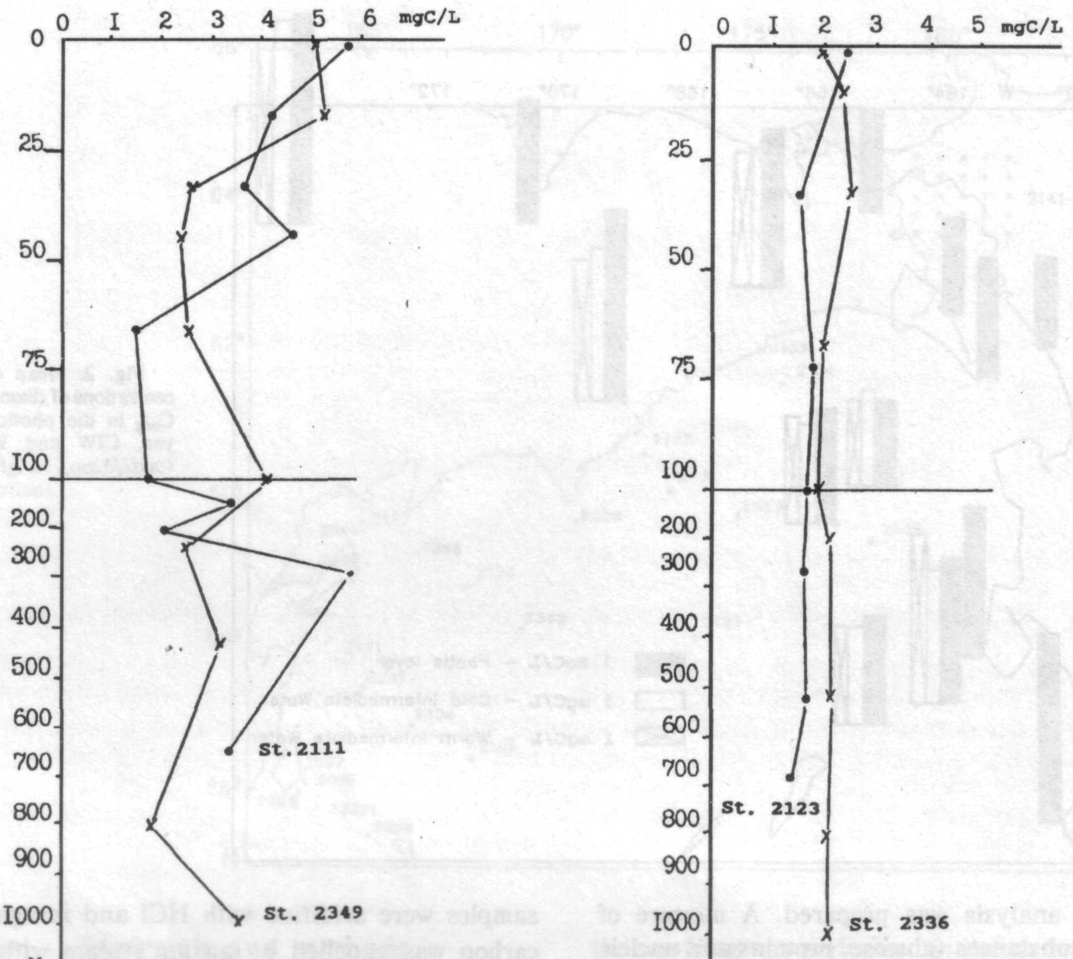


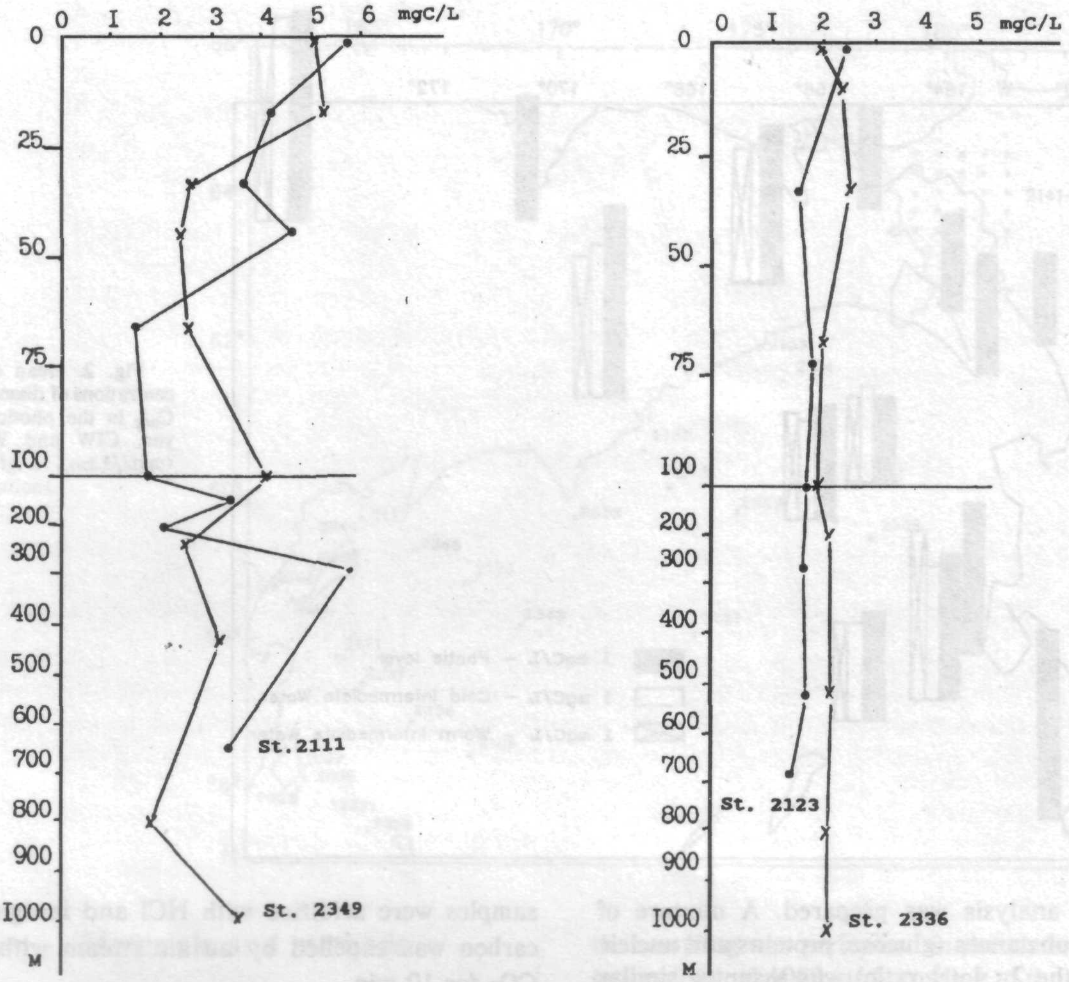
Fig. 3. Two patterns of vertical distribution of dissolved C_{org} (deep water stations).

From shelf further seawards the waters were marked by a tendency of an increase in OM concentrations in all three layers as well (Fig. 2).

The vertical distribution of DOM was fairly heterogeneous. A wide range of C_{org} concentrations could be observed not only in the photic layer, or in the surface 200 m layer, but even deeper. The data obtained at several deep water stations show a slight tendency to DOM decrease in deep layers. Though, the general pattern of the vertical distribution of DOM in the layer of 0-1000 m was characterized as a «zig-zag» one which was probably caused by different rates of biological processes at different depths. Unfortunately, the studies were carried out only in the layer of 0-1000 m. There were two main patterns of C_{org} vertical distribution along the whole layer of 0-1000 m with considerable variations in the values of C_{org} (maximal ΔC_{org} could equal 5.0 mgC/L). The second pattern was characterized by the presence of 2 maxima in the surface layer, a subsurface maximum in the layer of 10-30 m and a maximum on the photic layer boundary (40-70 m), and one or two maxima in the layer of 200-600 m. The low layer maxima were comparable to the surface ones. Both patterns were observed in the Kamchatka and Central basins (Fig. 3).

An even distribution of DOM with the concentrations of C_{org} of 3.0-3.4 mgC/L along the whole water column was observed in the coastal waters of the Karagin and Karyak shelves. Meanwhile, in the Kamchatka Strait the concentrations of C_{org} increased from the surface values of 1.0 mgC/L to 2.5 mgC/L at the depth of 25 m. The continental slope was also characterized by a slight increase of C_{org} concentrations with depth.

In the Anadyr Bay the distribution of dissolved C_{org} in the surface and bottom layers was scarcely influenced by the river discharge. Thus, surface and bottom concentrations were in the range of 3.4-4.3 mgC/L and 3.4-5.2 mgC/L, respectively, in the waters far seawards from the river discharge (Fig. 4, 5).



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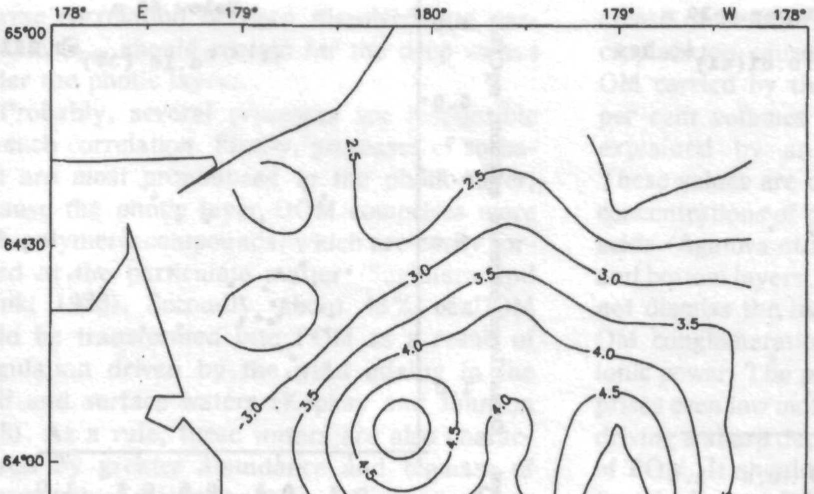

Fig. 4. Distribution of dissolved C_{org} in the surface layer of the Anadyr Bay (mgC/L).

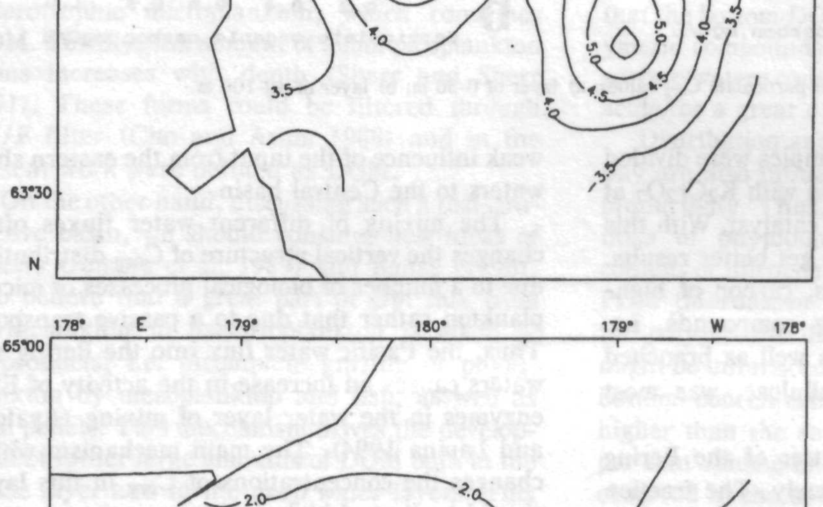

Fig. 5. Distribution of dissolved C_{org} in the bottom layer of the Anadyr Bay (mgC/L).

Discussion

The obtained mean concentrations of dissolved C_{org} are nearly 3.5 times higher than those reported by Loder (Loder 1971, Kinney et al. 1971) and 1.5-2.0 times higher than those obtained by Ljutsarev (Pashkova et al. 1988). These discrepancies could result from difference in the methods of sampling, filtration, handling and time of sample conservation, and, what is of most importance, different techniques of OM oxidation. Loder employed DOM oxidation with $K_2S_2O_8$ at 100°C, which resulted only in a small part of C_{org} complete oxidation. Ljutsarev deve-

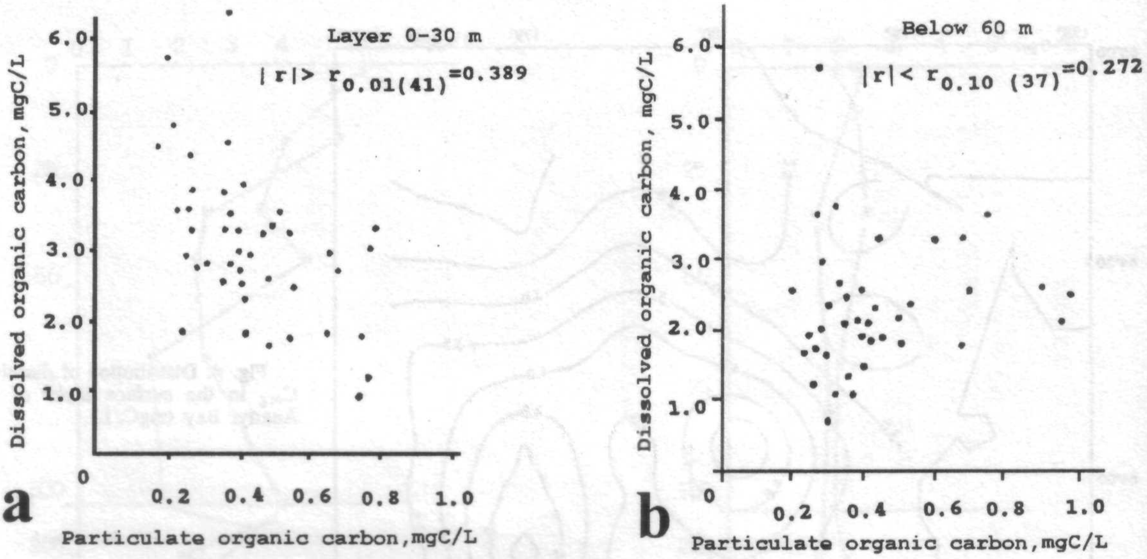

Fig. 6. Correlation of dissolved and particulate C_{org} values: a) layer of 0-30 m; b) layer of 40-100 m.

loped «tougher» conditions: samples were divided into fractions prior to oxidation with $K_2Cr_2O_7$ at 130°C; Ag_2SO_4 was used as a catalyst. With this method Ljutsarev managed to get better results. According to our observations, carbon of high-polymeric nitrogen-containing compounds, i.e. proteins and nucleic acids, as well as branched polymers, i.e. starch and cellulose, was most difficult to oxidize to CO_2.

The dissolved organic matter of the Bering Sea is hard to oxidize completely. The fraction of DOM which could be easily hydrolyzed makes up no more than 30%, and even less, by its total content.

The observed heterogeneous horizontal and vertical distribution of DOM could be caused by a number of hydrological, physico-chemical and biological factors (Lee and Wakeham 1989). We should attempt to identify the most important of those which influence the distribution of OM in the area of studies.

The heterogeneous nature of the horizontal and vertical distribution of OM is generally caused by hydrological features of the Bering Sea in the area of studies (Verkhunov et al. 1994). Thus, the bottom water flux from the Karagin Shelf to the Kamchatka Strait causes an increase in both dissolved and particulate C_{org} at the depth of 30-60 m (Agatova et al. 1994a). The Japanese investigators (Handa and Tanoue 1979) noted a similar increase in particulate C_{org} in the deep layers of the Aleutian basin and explained the phenomenon by OM transport from the continental shelf along the slope. Though, during the present studies the vertical distribution of both dissolved and particulate C_{org} was under rather weak influence of the input from the eastern shelf waters to the Central basin.

The mixing of different water fluxes often changes the vertical structure of C_{org} distribution due to a number of biological processes of microplankton rather that due to a passive transport. Thus, the Pacific water flux into the Bering sea waters causes an increase in the activity of ETS enzymes in the water layer of mixing (Agatova and Lapina 1994). The main mechanism which changes the concentrations of C_{org} in this layer should be that of biological processes.

The heterogeneous vertical distribution of DOM in the mesopelagic layer might be generally caused by bacterioplankton, especially the small (0.1 μm^3) free-living forms. Their biomass determines the observed maximal concentrations of dissolved OM in deep layers. Cho and Azam (1988) have observed an accumulation of picoplankton at the depth of 250 m and 600 m in the northern Pacific. They considered the activity of picoplankton to be responsible for keeping the balance between DOM and POM.

It should be also noted, that the shelf waters and the photic layer of the deep waters were characterized by an inverse relationship between the concentrations of particulate and dissolved C_{org} (Fig. 6a). Meanwhile, no correlation between them was observed below the depth of 100 m (Fig. 6b) (Agatova et al. 1994). Such a correlation between dissolved and particulate C_{org} was previously observed in the shelf waters of the Black Sea (Torgunova et al. 1992). A simple sorbation of DOM at the particulate matter, which can remove 10-30% of OM (Handa and Tanoue 1979, Abdel-Moati 1990) is unlikely to explain the phenomenon. If it were so, the inverse correlation between dissolved and particulate C_{org} should remain for the deep waters under the photic layer.

Probably, several processes are responsible for such correlation. Firstly, processes of sorbation are most pronounced in the photic layer, because the photic layer DOM comprises more high-polymeric compounds, which are easily sorbated at the particulate matter (Sugimura and Suzuki 1988). Secondly, about 43% of DOM could be transformed into POM as a result of coagulation driven by the wind mixing in the shelf and surface waters (Kepkay and Johnson 1988). As a rule, these waters are also characterized by greater abundance and biomass of heterotrophic microplankton, which consumes DOM. Thirdly, the amount of small picoplankton forms increases with depth (Sherr and Sherr 1991). These forms could be filtered through GF/F filter (Cho and Azam 1988) and in the present work were defined as DOM.

On the other hand, discussing such a fish-productive basin, we should consider new ideas of Jumars (Jumars et al. 1989) and Banse (1990), who believe that a great part of OM flux from phytoplankton to bacterioplankton is made of by-products, i.e. incomplete grazing of phytoplankton by mezoplankton and fish, as well as fecal pellets. This mechanism drives the development of rather large amounts of DOM both in the photic layer and in the deep water layers. This mechanism is probably the main one in the Kamchatka Strait and the Kamchatka Basin. This hypothesis could be confirmed by the fact that minimal ratio values of C/N and C/P were observed in the waters under the photic layer, and the bacterial transformation of DOM from POM resulted in the input of C_{org}, but not N_{org}, or P_{org} (Karl et al. 1991).

Quantitative variability of DOM in the ecosystem of the Anadyr Bay is generally caused by two processes. The first one is a physico-chemical process of flocculation. The second one is a development of biological barrier, i.e. the increase of heterotrophs in the population of microplankton causes high rates of the uptake of OM carried by the river discharge. Thus, high per cent volumes of POM and DOM could be explained by an outburst of microplankton. These values are confirmed by the data on high concentrations of particulate proteins and nucleic acids (Agatova et al. 1994b), both in the surface and bottom layers. On the other hand, one should not dismiss the influence of the development of OM conglomeration due to the changes of the ionic power. The process of conglomeration comprises even low molecular OM (flocculation), thus driving a sharp decrease of DOM and an increase of POM. It should be not considered accidental that the bottom DOM practically has no high-polymeric compounds, i.e. nucleic acids, while the surface waters contain either no dissolved nucleic acids, or a great deal of particular ones.

Distribution and nature of OM in the Anadyr Bay are also influenced by the rates of primary productivity. Thus, the areas of high concentrations of phytopigments are marked by high content of nitrogen and phosphorus in DOM and POM (Mordasova 1994). In the eastern part of the polygon the distribution and nature of OM might be influenced by flocculation processes: the bottom concentrations of POM are 2-7 times higher than the surface ones, and the maximal per cent volume of POM by DOM (51-105%) is observed in the bottom layer.

Thus, in the Bering Sea the mean summer concentrations of dissolved C_{org} equal 3-4 mgC/L in the layer of 0-1000 m, which are two times higher than the data previously published. The highest concentrations hold for the regions of high productivity at all trophic levels of the Bering Sea ecosystem.

Acknowledgements

The investigations were carried out with the financial support of the Russian Foundation for Fundamental Research, Programs No. 93-05-8336 and No. 93-05-8335.

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Растворенное органическое вещество Берингова моря

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РЕЗЮМЕ. Представлены данные по горизонтальному и вертикальному распределению растворенного C_{org}, концентрации которого определены методом высокотемпературного каталитического сожжения в токе кислорода на TOC-500. Значения величин находятся в пределах 1.5-6.0 мгС/л. Минимальные значения единичны. Пространственное распределение очень неоднородно, и в основном определяется интенсивностью продукционно-деструкционных процессов. В Анадырском заливе в распределении растворенного C_{org} большое значение приобретает физикохимический процесс флокуляции.

Растворенное органическое вещество Берингова моря с трудом поддается полной минерализации. Легко гидролизуемая фракция его составляет не более 30%. Наиболее трудно поддается полному окислению углерод, входящий в состав высокополимерных азотсодержащих соединений типа белков и нуклеиновых кислот.